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(54) **Method of reducing NO<sub>x</sub> emissions from lean-burn combustion engines**

(57) The invention includes an operating strategy for zeolite-based catalysts used for reduction of NO<sub>x</sub> from highly lean exhaust conditions. The invention includes a method to enhance the high temperature activity of zeolite-based catalysts by modifying the transient feed composition without changing the overall time-average feed composition. More specifically, a cyclic operation method with alternating feed conditions between rich and lean to enhance the activity of zeolite-based catalysts to remove NO from lean exhaust gases when the overall exhaust composition contains a large amount of excess oxygen, without affecting the catalysts' activity to remove hydrocarbons. The rich to lean transient conditions are created by periodically adding hydrocarbon pulses from a different source to the combustion emissions.

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**Description****Field of the Invention**

5 This invention relates to methods of controlling combustion engine emissions, and more particularly to a method of reducing NO<sub>x</sub> and emissions from a lean-burn combustion engine.

**Background of the Invention**

10 Diesel and lean-burn gasoline engines generally operate under highly oxidizing conditions (i.e., using much more than is necessary to burn the fuel), typically at air/fuel ratios greater than 17, and usually about 20 to 23. Under these highly lean conditions, typical three-way catalysts (for converting hydrocarbons, NO<sub>x</sub> and CO containing primarily noble metals such as Pt, Pd, and Rh supported on γ-alumina exhibit little activity toward NO<sub>x</sub> reduction, as their reduction activity is suppressed by the presence of excess oxygen. Recently, copper-ion exchanged zeolite catalysts, especially  
 15 Cu-ZSM-5 catalysts among others, have been shown to be active for selective reduction of NO<sub>x</sub> by hydrocarbons in the presence of excess oxygen. Platinum-ion exchanged zeolite catalyst, such as Pt-ZSM-5 is also known to be active for NO<sub>x</sub> reduction by hydrocarbons under lean conditions. However, this catalytic activity is significant only in a narrow temperature range around the lightoff temperature of hydrocarbon oxidation. All the known lean-NO<sub>x</sub> catalysts reported in the literature tend to lose their catalytic activity for NO<sub>x</sub> reduction when the catalyst temperature reaches well above  
 20 the lightoff temperature of hydrocarbon oxidation. This narrow temperature window of the lean-NO<sub>x</sub> catalysts is considered to be one of the major technical obstacles, because it makes practical application of these catalysts difficult for lean-burn gasoline or diesel engines.

The present invention overcomes many of the shortcomings of the prior art.

**SUMMARY OF THE INVENTION**

The invention includes an operating strategy for zeolite-based catalysts used for reduction of NO<sub>x</sub> from highly lean exhaust conditions such as from both diesel and gasoline engines. The invention includes a method to enhance the high temperature activity of zeolite-based catalysts by modifying the transient composition of feed to the reactor without  
 30 changing the overall time-average feed composition. More specifically, a cyclic operation method is used with alternating feed conditions between rich and lean to enhance the activity of zeolite-based catalysts to remove NO<sub>x</sub> from lean exhaust gases. The rich to lean transient conditions are created by periodically introducing hydrocarbon pulses to the reactor from a source different than the combustion emissions. The hydrocarbon may also be added at a constant rate.

35 These and other objects, features and advantages of the present invention will become apparent from the following detailed description and appended claims.

**Detailed Description**

To make the lean-NO<sub>x</sub> catalysts such as Cu-ZSM-5 and Pt-ZSM-5 practicable to the real emission control application,  
 40 it is therefore important to improve the overall catalytic activity of those catalysts. One way to achieve this is to widen the effective temperature window of the catalysts by improving the catalytic activity at high temperatures above the lightoff temperature of hydrocarbon oxidation. A method of expanding the temperature window of the lean-NO<sub>x</sub> catalysts for NO<sub>x</sub> reduction activity can be identified by thorough understanding of the unique reaction dynamics of NO<sub>x</sub> reduction by hydrocarbons in the presence of excess oxygen, which is characteristic of the zeolite-based lean-NO<sub>x</sub> catalysts.  
 45 During our recent investigation of the transient reaction dynamics of the lean-NO<sub>x</sub> catalysis, we have made two discoveries of practical importance. One is that the zeolite-based lean-NO<sub>x</sub> catalysts can store substantial amounts of hydrocarbons even at high temperatures up to around 500°C, and the other is that the maximum catalytic activity for NO<sub>x</sub> reduction can be achieved during the transition between rich and lean conditions. These two discoveries are the key concepts employed in this invention to improve the overall performance of the lean-NO<sub>x</sub> catalysts. This invention is  
 50 concerned with an operating strategy of lean-NO<sub>x</sub> catalysts, by which the activity of lean-NO<sub>x</sub> catalysts can be improved and the temperature window of the catalysts for NO<sub>x</sub> reduction can be widened. More specifically, it has been discovered that an appropriate cyclic operation of the lean-NO<sub>x</sub> catalysts can markedly improve the overall performance of the catalysts for NO<sub>x</sub> reduction under highly lean conditions at temperatures above the reaction lightoff temperature.

Under steady-state operating conditions, the temperature range where the NO<sub>x</sub> reduction activity of the lean-NO<sub>x</sub>  
 55 catalysts can be well utilized is confined to a narrow temperature window around the lightoff temperature of hydrocarbon oxidation. Above this temperature, the conversion of hydrocarbons reaches near completion. As temperature rises above the lightoff temperature of hydrocarbon oxidation, the catalysts gradually loses their catalytic activity due to the lack of hydrocarbons which can prevent the active catalytic sites from being poisoned by the excess oxygen.

Under cyclic operating conditions between rich and lean conditions, on the other hand, the zeolite-based lean-NO<sub>x</sub> catalysts can store hydrocarbons during the rich half-cycle and release them during the subsequent lean half-cycle. By this periodic cycling operation, deactivation of the catalysts due to the excess oxygen can effectively be prevented from occurring. Consequently, the temperature window of the catalysts under the cyclic operating condition becomes much wider than that under the steady-state operating condition. This results in a significant improvement in the overall performance of the lean-NO<sub>x</sub> catalysts. Experimental demonstrations of this concept are presented below.

In order to compare the effectiveness of cyclic operation of our invention with that of conventional steady state operations, we carried out a series of reactor experiments using both Cu-ZSM-5 and Pt-ZSM-5 catalysts. Details of experimental conditions are listed in Table 1.

Table 1

Standard Experimental Conditions	
Cu-ZSM-5 Catalyst:	Si/Al ratio = 32 Cu loading = 2.4 wt %
Pt-ZSM-5 Catalyst:	Si/Al ratio = 40 Pt loading = 0.5%
Reactor:	0.32 cm o.d. stainless steel tubing Catalyst particle size = 80-120 mesh Sample weight = 0.015 g Catalyst bed length = 1 cm Total gas flow rate = 50 cm <sup>3</sup> /m (STP) Gas space velocity = 86,000/h Temperature = 200-600°C Pressure = 101.3 kPa (1atm)
Feed Concentration:	C <sub>2</sub> H <sub>4</sub> = 1200 ppm NO = 230 ppm O <sub>2</sub> = 7 % He = balance

ZSM-5 zeolite powder samples in the size range of approximately 0.5-1 μm were obtained from PQ Corporation, which had high Si/Al ratios of approximately 32 and 40. The Cu-ZSM-5 and Pt-ZSM-5 catalysts were prepared by ion exchange of copper and Pt on the ZSM-5 zeolite to obtain a copper loading of 2.4 weight percent and Pt loading of 0.5 weight percent, respectively. The ion-exchanged ZSM-5 samples were dried overnight in air at room temperature, heated slowly in flowing air up to 500°C, and then calcined in air at 500°C for four hours. The Cu-ZSM-5 and Pt-ZSM-5 powder samples were made into disks by compressing at 10 ton pressure. The resulting sample disks were crushed, ground, and screened for 80-120 mesh sizes to be used for reactor experiments.

A fixed-bed reactor was prepared using a 3.2 mm O.D. stainless steel tube. The depth of the catalyst bed in the tube was 1 cm. The reactor was placed in a 30 cm long tubular furnace, and the reactor temperature was measured at the inlet of the catalyst bed and controlled electronically with a typical precision of ± 1°C. Before each experimental run for activity measurement, the reactor containing the catalyst particles was flushed with 7 volume percent oxygen in helium at 600°C for two hours to burn off any carbonaceous deposits on the catalytic surface. The reactor temperature was then reduced to the desired operating temperatures. The apparatus was designed in such a way that both steady-state experiments and transient cycling experiments could be performed. The total gas flow rate was 50 cm<sup>3</sup>/minute at 101 kPa. The transient responses of the gas-phase concentration in the exit stream from the reactor were monitored as a function of time by a mass spectrometer.

The catalytic activity of both Cu-ZSM-5 and Pt-ZSM-5 catalysts under steady-state operating conditions was compared with that under cyclic operating conditions, with the time-average feed composition being kept constant. Under the steady-state operating conditions, the standard reaction mixture (i.e., NO+C<sub>2</sub>H<sub>4</sub>+O<sub>2</sub>) was steadily fed to the reactor. Under the cyclic operating conditions, a pulse of 20 second duration containing C<sub>2</sub>H<sub>4</sub>+NO+Ar (rich half-cycle) was introduced to the reactor, followed by an oxygen pulse of the same duration (lean half-cycle). This rich/lean cycling process

was repeated until the system was stabilized. The feed concentrations of NO, ethylene and oxygen were 230 ppm, 1200 ppm and 7 percent, respectively, for both the steady-state and the cyclic operating conditions. Note that the overall time-average feed composition remained in the highly lean condition for both the steady-state and the cyclic operating conditions. Argon was used as an inert reference gas to help identify the half-cycle that contained NO and ethylene in the feed. The conversion of NO was measured by a mass spectrometer.

Results shown in Table 2 are time-average conversion of NO to nitrogen over Cu-ZSM-5 catalyst at three different temperatures above the lightoff temperature of C<sub>2</sub>H<sub>4</sub> oxidation which was found to be 325°C. They clearly indicate that the activity of the Cu-ZSM-5 catalyst for nitric oxide reduction can be enhanced by operating the catalyst in a cyclic mode instead of the traditional steady-state mode. The conversion of C<sub>2</sub>H<sub>4</sub> remained the same under both operating conditions.

Table 2

Performance of Cu-ZSM-5 Catalyst		
Temperature	Conversion of NO to N <sub>2</sub>	
	Steady Operation	Cyclic Operation
350°C	68.3 %	72.0 %
400°C	49.0 %	76.2 %
500°C	23.6 %	92.6 %

The same trend was observed for the Pt-ZSM-5 catalyst as shown in Table 3, without affecting the conversion of C<sub>2</sub>H<sub>4</sub>. The reaction lightoff temperature of C<sub>2</sub>H<sub>4</sub> oxidation was found to be 215°C for Pt-ZSM-5, much lower than that for Cu-ZSM-5.

Table 3

Performance of Pt-ZSM-5 Catalyst		
Temperature	Conversion of NO to N <sub>2</sub>	
	Steady Operation	Cyclic Operation
300°C	37.3 %	64.1 %
500°C	2.4 %	72.1 %

Effects of hydrocarbon addition to the standard feed mixture on the NO<sub>x</sub> conversion efficiency of lean-NO<sub>x</sub> catalysts were examined by introducing additional C<sub>2</sub>H<sub>4</sub> to the standard feed stream either in a steady-addition mode or in a cyclic-addition mode. Results are shown in Table 4 and 5.

Table 4

Effect of C <sub>2</sub> H <sub>4</sub> Addition on Performance of Cu-ZSM-5 Catalyst		
Mode of C <sub>2</sub> H <sub>4</sub> Addition	Conversion of NO to N <sub>2</sub>	
	375°C	500°C
No Addition	64.1 %	23.6 %
Steady Addition	71.9 %	26.5 %
Cyclic Addition	84.4 %	31.2 %

Table 5

Effect of C <sub>2</sub> H <sub>4</sub> Addition on Performance of Pt-ZSM-5 Catalyst	
Mode of C <sub>2</sub> H <sub>4</sub> Addition	Conversion of NO to N <sub>2</sub> at 500°C
No addition	2.4 %
Steady Addition	9.2 %
Cyclic Addition	15.7 %

In the no-addition mode (Table 4 and 5), the standard feed mixture was composed of 230 ppm NO<sub>x</sub>, 1200 ppm C<sub>2</sub>H<sub>4</sub> and 7 percent O<sub>2</sub>, as shown in Table 1. In the steady-addition mode, a steady flow of C<sub>2</sub>H<sub>4</sub> (5000 ppm in He) was introduced at a rate of 5 cc/minute to the standard feed mixture. In the cyclic-addition mode, a pulse of C<sub>2</sub>H<sub>4</sub> (5000 ppm in He) was introduced for a duration of 10 seconds at a rate of 10 cc/minute, followed by the flow of the standard feed mixture for the next 10 seconds by cutting off the additional C<sub>2</sub>H<sub>4</sub> flow. This cyclic addition of C<sub>2</sub>H<sub>4</sub> was repeated until the reaction system was stabilized. Note that the time-average amount of C<sub>2</sub>H<sub>4</sub> added to the standard feed stream is the same for the steady-addition and the cyclic-addition mode. Results for the Cu-ZSM-5 catalyst presented in Table 4 led us to two important findings. First, the catalytic activity of Cu-ZSM-5 above the reaction lightoff temperature can be improved by addition of hydrocarbons, particularly C<sub>2</sub>H<sub>4</sub>. Second, cyclic addition of C<sub>2</sub>H<sub>4</sub> is more effective for NO reduction than steady addition for the same amount of C<sub>2</sub>H<sub>4</sub> addition. In all cases, the conversion of C<sub>2</sub>H<sub>4</sub> remained constant at 100% conversion. The same trend was observed for the Pt-ZSM-5 catalyst, as shown in Table 5.

The active catalytic metal ingredients can be Pt, Rh, Pd, Cu, Ni, Co, Cr, Fe, Mn, rare earth metals, etc., while the catalyst support can be various types of zeolites such as ZSM-5, mordenite, zeolite, etc., depending on the type of hydrocarbons available in the reaction system.

The hydrocarbons useful in the cyclic process of the present invention can be C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, CH<sub>4</sub>, etc., depending on the type of the active catalytic ingredients and the operating conditions. The cyclic addition of hydrocarbon pulses to the standard feed stream achieves maximum enhancement of the catalytic activity. The pulse duration can be varied for the optimum performance, preferably in the range of 1 second through 60 seconds. Pressure of the additional hydrocarbon pulses can be in a slight positive pressure with respect to the standard feed pressure, preferably in the range of 0.1 to 10 psi. A lean burn gasoline engine may be operated at 17 to 20 to 23 air/fuel ratios. A diesel engine may be operated at an air/fuel ratio ranging from 35 to 45.

#### Claims

1. A method comprising:  
operating a combustion engine at an air/fuel ratio greater than 17, collecting the exhaust from the combustion engine in an exhaust system including a zeolite-based material having a catalyst thereon;  
cyclically adding hydrocarbons from a source other than the combustion engine to the exhaust in the exhaust system prior to the exhaust flowing over the catalyst and wherein said catalyst has an operating temperature ranging from light-off temperature to about 500°C.
2. A method as set forth in claim 1 wherein said catalyst comprises copper.
3. A method as set forth in claim 1 wherein said catalyst comprises platinum.
4. A method as set forth in claim 1 wherein said catalyst comprises a noble metal.
5. A method as set forth in claim 1 wherein said catalyst is deposited on said zeolite-based material by ion-exchange.
6. A method as set forth in claim 1 wherein the combustion engine is a gasoline engine operated at an air/fuel ratio of greater than 17 to about 23.
7. A method as set forth in claim 1 wherein said combustion engine is a diesel engine and the air/fuel ratio is 35 to 45.

8. A method to enhance the high-temperature activity of zeolite-based catalysts for  $\text{NO}_x$  removal from combustion exhaust gas by modification of the exhaust composition through constant addition of hydrocarbons, without affecting the catalysts' activity for hydrocarbon removal.

5 9. A method to enhance the activity of lean- $\text{NO}_x$  catalysts for  $\text{NO}_x$  removal by modification of the exhaust composition through periodic addition of hydrocarbon species, without affecting the catalysts' activity for hydrocarbon removal.

10. A method of creating temporarily fuel-rich conditions around the catalyst particles, even when the standard exhaust composition is in a highly fuel-lean condition, by periodic addition of strong hydrocarbon pulses to the reactor.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 95 20 2584

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 503 882 (TOYOTA JIDOSHA KK) * column 3, line 7 - line 41 * * column 6, line 51 - column 8, line 35; claims 1-12; figures 2,3 *	1-10	B01D53/94
X	EP-A-0 483 715 (IDEMITSU KOSAN CO. LTD.) * page 4, line 20 - line 47; claims 1-5 *	1,2,5-10	
X	US-A-5 149 511 (FORD MOTOR CO.) * column 2, line 31 - column 3, line 68; claims 1-9 *	1-9	
X	US-A-5 254 322 (MOBIL OIL CORP.) * column 4, line 55 - column 5, line 27; claims 1-8 *	1-6,8,9	
X	EP-A-0 351 197 (JOHNSON MATTHEY PLC) * page 2, line 38 - page 3, line 7; claims 1-10 *	10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31 January 1996	Examiner Eijkenboom, A
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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